Onderzoek naar het bestaan van IC12+-ionen

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SUMMARY

Emeléus and his coworkers have shown that a number of interhalogen compounds react with halogenides to give complex compounds in which positive or negative polyhalogen ions occur. Typical examples are:

$$BrF_3 + SbF_5 \rightarrow BrF_2^+ + SbF_6^-$$
$$BrF_3 + AgF \rightarrow Ag^+ + BrF_4^-$$

Of the polyhalogen ions ICl_2^+ and ICl_4^-, which may possibly be derived from the interhalogen compound I_2Cl_6, only ICl_4^- ions were known. The present investigation was undertaken to determine whether also ICl_2^+ions can exist under certain conditions.

Initially the nature of the relatively high conductivity of molten ICl and of solid I_2Cl_6, reported bij Greenwood and Emeléus (1950) was investigated. It was shown that ICl_2^+ions are not involved in the conduction of molten ICl. In contrast to the results of Greenwood and Emeléus, solid I_2Cl_6 was found to show only a very small conductivity near the melting point.

Next, attempts were made to prepare compounds which might contain ICl_2^+ions. To this end I_2Cl_6 was heated with $SbCl_5$, Al_2Cl_6, $PtCl_4$, $SnCl_4$ and BCl_3 respectively. It was found that I_2Cl_6 reacts with $SbCl_5$ and Al_2Cl_6 to give the compounds $ISbCl_8$ and $IAlCl_6$, which are crystalline substances at room temperature. From the properties of molten $ISbCl_8$ and of solutions of $ISbCl_8$ in $POCl_3$ and liquid SO_2 it followed, that under these circumstances no appreciable dissociation of the form $ISbCl_8 \rightarrow ICl_2^+ + SbCl_6^-$ takes place. In carbon tetrachloride solution $ISbCl_8$ is probably completely decomposed into ICl, Cl_2 and $SbCl_5$.

Finally, the crystal structure of $ISbCl_8$ and $IAlCl_6$ were determined by means of X-ray diffraction. The structure of $ISbCl_8$ (fig. V, 1) consists of ICl_2^+ions with an approximately rectangular shape and of $SbCl_6^-$ions which show slight, but significant deviations from octahedral symmetry. The ICl_2^+ and $SbCl_6^-$ions are linked in chains by weak covalent bonds. The interatomic distances and bond angles in these chains (fig. V, 3) can be explained in a qualitative way by assuming a mesomerism between the structures $[ICl_2]^+[SbCl_6]^-$ and $[ICl_4]^-[SbCl_4]^+$ of which the structure $[ICl_2]^+[SbCl_6]^-$ predominates.

In the $IAlCl_6$-crystals (fig. V, 4, 5) chains of ICl_2^+ions and $AlCl_4^-$ions occur, of which the former are similar to the ICl_2^+ions in $ISbCl_8$, whereas the $AlCl_4^-$ions have an approximately tetrahedral configuration. In these chains a mesomerism was assumed between

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Experimental details

The nature of the conductivity of molten ICl was studied by means of electrolysis, followed by a quantitative determination of the changes in the composition in the liquid near the electrodes (III, 2). These changes were in favour of the dissociation scheme (c), page 19.

It was suspected that the conductivity of „solid" I_2Cl_6, observed by Greenwood and Emeléus had been caused by a liquid phase due to decomposition of I_2Cl_6 into ICl and Cl_2, which occurs when I_2Cl_6 is heated in a sealed tube. During a reinvestigation of the conductivity of solid I_2Cl_6 (II, 1) this decomposition was prevented by applying a suitable Cl_2-pressure. Under these circumstances I_2Cl_6 melted sharply at 98,5 °C, while the conductivity increased from some value below $10^{-6}\ \Omega^{-1}\,cm^{-1}$ to $8{,}5 \times 10^{-3}\ \Omega^{-1}\,cm^{-1}$.

The compounds $ISbCl_8$ (II, 3) and $IAlCl_6$ (II, 4) were obtained by heating I_2Cl_6 with $SbCl_5$ and Al_2Cl_6 respectively in sealed tubes. Also, $ISbCl_8$ was prepared by passing a stream of Cl_2 into a solution of ICl in $SbCl_5$. Both $ISbCl_8$ and $IAlCl_6$ loose ICl and Cl_2 on heating under normal pressure.

During the measurements of the conductivity of molten $ISbCl_8$ (II, 5) a Cl_2 pressure of about 18 atm. was applied. Under these circumstances $ISbCl_8$ melted sharply at 83,5 °C without previous decomposition. The log $\varkappa$ versus 1/T curve for the molten compound is shown in fig. II, 3. The observed conductivity is too low for complete dissociation of $ISbCl_8$ into ICl_2^+ and $SbCl_6^-$ ions, but it might be explained by decomposition of $ISbCl_8$ into $SbCl_5 + {}^1/_2\ I_2Cl_6$ or $SbCl_5 + ICl + Cl_2$.

The conductivity of a solution of $ISbCl_8$ in liquid SO_2, together with the conductivities of some related substances in liquid SO_2, are shown in table II, 1. Apparently in this solvent $ISbCl_8$ does not show an ionic character like the other chloroantimonates.

A solution of $ISbCl_8$ in $POCl_3$ exhibited appreciable conductivity (II, 6). From a measurement of the iodine transport during electrolysis it followed that the iodine atoms in this solution are either bound in molecules or in anions with a low transport number.

Evidence for complete dissociation of $ISbCl_8$ into ICl, Cl_2 and $SbCl_5$ in carbon tetrachloride solution was obtained from a comparison of the UV absorption spectra of solutions of $ISbCl_8$, ICl, Cl_2 and $SbCl_5$ in carbon tetrachloride.

Chapter III deals with the determination of the crystal structure

of $ISbCl_8$ by means of X-ray diffraction. The crystals were found to be tetragonal, $a = 6{,}98$ Å, $c = 24{,}2$ Å, with the spacegroup $P4_1$ or $P4_3$, and with 4 $ISbCl_8$ units per unit cell. Integrated and non-integrated Weissenberg photographs were taken with Zr-filtered Mo radiation. The intensities of 68 reflections $hk0$ and 162 reflections $h0l$ were recorded; the latter were corrected for absorption. The Sb- and I-atoms were located from Patterson syntheses of the two independent projections. The signs of a number of structure-factors $hk0$ and approximate values of the phase angles of the structure-factors $h0l$ were determined from the contributions of the Sb- and I-atoms. Fourier syntheses of the projections, of which the non-centrosymmetric one is shown in fig. III, 3, served to locate the Cl-atoms. The atomic coördinates were refined in four steps of $h0l$ structure-factor calculation and Fourier syntheses of the [010] projection. A survey of the refinement is given in table III, 1; the final coordinates are listed in table III, 2. The $hk0$ structure-factors were not used in the determination of these coordinates as too many atoms were partially overlapped by others in the [001] projection. The standard deviations of the coordinates were estimated as 0,007, 0,007 and $0{,}03_5$ Å for the Sb, I and Cl atoms respectively.

The determination of the crystal structure of $IAlCl_6$ is described in Chapter IV. $IAlCl_6$ crystallizes in the monoclinic spacegroup $P2_1$, with two $IAlCl_6$ units per unit cell. The cell dimensions are $a = 6{,}92$ Å, $b = 11{,}02$ Å, $c = 6{,}11$ Å and $\beta = 99{,}1°$. Weissenberg photographs of the reflections $0kl$ and precession photograps of the reflections $hk0$ and $h0l$ were obtained with Zr-filtered Mo radiation. The intensities of 88 reflections $0kl$, of 66 reflections $h0l$ and 76 reflections $hk0$ were used in the determination of the structure. The positions of the I atoms were readily found from Patterson syntheses of the projections. The domination of the contributions of the I atoms to the structure-factors was used to locate the Cl and Al atoms. Refinement of the atomic coordinates proceeded according to standard procedures. In the last stage of the refinement one set of atomic coordinates was used in a calculation of the structure-factors for all three projections, after which the information obtained from subsequent $F_{obs} - F_{cal}$ syntheses was combined to determine the final coordinates. Values of the temperature coefficients and the disagreement indices are given in table IV, 4; the final coordinates are listed in table IV, 5. The estimated standard deviations of the atomic coordinates are 0,006, $0{,}03_5$ and $0{,}04_5$ Å for the I, Cl and Al atoms respectively.

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